



## Investigation of a novel soil analysis method in agricultural areas of Çarşamba plain for fertilizer recommendation

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### Abstract

In this study, a novel soil analysis method for fertilization recommendation was developed and validated with 161 soil samples taken from Turkey - Çarşamba plain for determination of potassium as a plant nutrient. In conventional soil analysis methods, available potassium (K) nutrient was determined by ammonium acetate extraction with flame photometer. In this study an alternative to existing method was proposed by developing extraction solutions suitable for interference dynamics of ion selective electrodes in a flow injection setup. Flow injection analysis system was optimized and K ion concentration of 161 soil samples taken from Turkey - Çarşamba plain was determined with potentiometrically. For the same soil samples, K<sup>+</sup> ion concentration was determined with ammonium acetate extraction using flame photometer in parallel. Fertilization recommendations for potassium was calibrated on ammonium acetate extraction based measurements. In order to evaluate available potassium nutrient analysis results from new generation soil analysis method in fertilization recommendation process, a correlation model is required for relating new generation method results to conventional method results. An artificial neural network based soft sensor system was developed for this task. Potentiometric K<sup>+</sup> ion measurement of soil sample in flow injection analysis system was presented as input to soft sensor system. Soft sensor predicted available K in soil sample based on artificial neural network model which can be used in fertilizer recommendation. Prediction performance of soft sensor was validated with experimental data and fitted with high correlation coefficient (R<sup>2</sup>= 0.902). Experimental studies have shown that K determined by potentiometric measurements can be used in fertilization recommendations in Çarşamba plain by using soft sensor approach..

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### Introduction

Spectrophotometric devices such as flame photometer, ICP-OES (inductively coupled plasma atomic emission spectroscopy) UV and AAS (atomic absorption spectrophotometer) are widely used in standard soil agricultural analysis that aimed at fertilizer recommendation. Advanced analysis devices like ICP-OES allow simultaneous measurement of different species from a single sample of soil extract (Bortolon et al., 2011). On the other hand these devices have considerably high initial investment and operating cost. In addition size and fragility of such devices makes transportation difficult thus makes their usage for on-field analysis unsuitable.

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It is important for both economy and environmental health that fertilization recommendation is based on soil analysis so that required amount of fertilizer is determined precisely. A mobile soil analysis system that can give rapid results on the field can be a cost-effective solution. In present, agriculture technology has advanced to a new stage that usage of mobile soil analysis systems in precision agriculture is commercially viable.

Recently, electrochemical ion-selective electrodes (ISE) with benefits of low-cost, accuracy, easy utilization and transportable are studied as an alternative to conventional soil analysis methods (Sethuramasamyraja et al., 2008; Adamchuk et al., 2005; Adamchuk et al., 2004; Lobsey, 2010). There are various studies in literature showing that ion-selective electrodes can be utilized in soil analysis (Kim et al., 2007; Birrell et al., 2001; Wang et al., 2001; Cieřła, 2007).

The parameters required for fertilizer recommendation are available forms of nutrient elements required by crop, pH, salt and lime. Determination of these parameters depend on specific extraction and measurement methods which developed by field calibration studies specific to the local region. Any developed soil analysis method must be correlated with conventional soil analysis method in order to be utilized in fertilizer recommendation calculations. Correlation could be based on a linear model with a single correlation coefficient or a non-linear model for complex relation between traditional calibrated method and novel method.

In industrial processes, it is common that measurement of some of crucial process parameters exhibit difficulties such as high financial cost, significant delay in measurement. In some cases, there can be no hardware sensor for directly measuring primary process variable of interest. Soft sensors are employed to predict primary process variables by utilizing measurements of secondary variables and a mathematical model. Mathematical model can be formed by using first-principals or can be a data driven model. Data driven models depend on a soft computing techniques such as artificial neural networks, decision trees, fuzzy logic or support vector machines (Lin et al., 2007). Performance of a soft sensor mainly depends on selection of input variables and soft sensing model. Secondary variables that have been chosen as input to soft sensor must be related to the primary variable. Colinearity between input variables may deteriorate accuracy of soft sensor (Dufour et al., 2005). In complex systems, soft sensing model structure must have adequate complexity for description of non-linear relationship between primary variable and soft sensor input variables.

In this study, a novel soil analysis method has been established by development of a flow injection analysis system using ion-selective electrodes as detector with appropriate extraction solutions. This analysis system can be used on-field for soil analysis and can provide a low cost solution for fertilizer recommendation procedures. Correlation model required between proposed analysis system and conventional soil analysis method has been established by soft sensor approach using an artificial neural network model. Soft sensor has been tested for measurement of available potassium and corresponding fertilizer recommendation.

## Material and Methods

A total of 161 soil samples analyzed with conventional standard methods and developed soil analysis system. Input and output data set for training of soft sensor model was derived from obtained analysis results.

### Sampling Points

Soils used in this study were gathered from arřamba plain which is located in city of Samsun, Turkey (Figure 1). A total of 161 soil samples from arřamba were selected to represent the diverse soil characteristics of important agricultural areas of arřamba and to provide a wide range of K concentration levels. Total area covered by sample coordinate points was 101131 hectare. Texture property distribution of collected samples was found to be 44% clay, 18% clay loam, 8% sandy clay loam, 3% sandy loam, 9% silt clay, 9% silt clay loam, 9% loam.

Soil samples were gathered from 0-20 cm of depth, and prepared for analysis by drying at room temperature (25  C) and sieving with a 2 mm sieve.

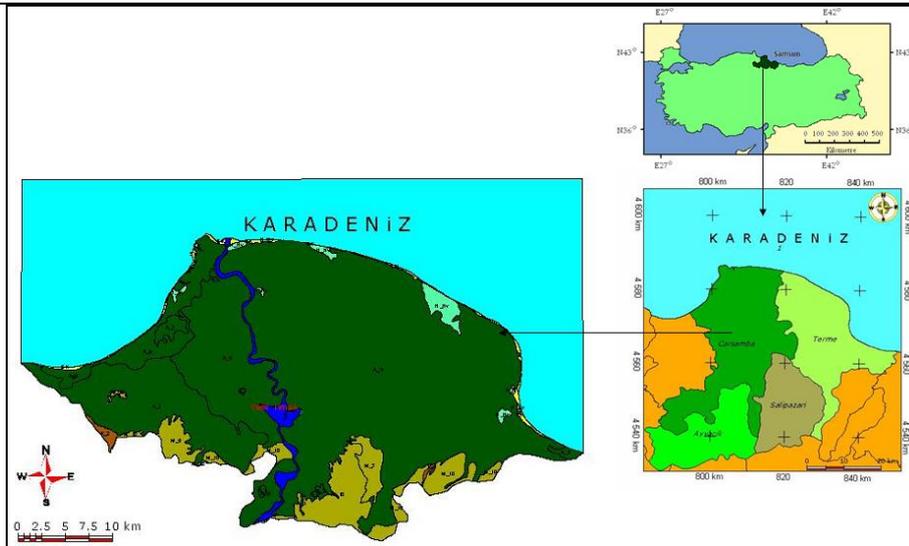


Figure 1. Soil map of Çarşamba plain where samples were collected

### Soil Extraction and Measuring

For conventional soil analysis, available potassium content was determined by mixing 1 N Ammonium acetate solution with soil sample and leaving for one night. This procedure was the same procedure employed in field calibration studies in that region. Output of this analysis results were used as target primary variable in building of soft sensor model.

Input variables of soft sensor were nutrition element content measured by ion-selective electrodes in flow-injection analysis system. Flow injection analysis system used in this study was developed in our research laboratory (Figure 2). Additionally, soil texture content, pH, EC and Lime were also used as input variables. In optimization of soft sensor model, a subset of these input variables was selected to improve performance.

In Figure 2, a mini circulation pump (Welco, WP100) provided continuous flow in the system. For sample injection a 3-way valve (The Lee Company) was used. As mentioned above, ion selective electrodes specific to 4 different nutrition element ( $K^+$ ,  $Ca^+$ ,  $NH_4^+$ ,  $NO_3^-$ ) were employed in detection unit. Sample holder was designed in-house and made of plexiglass. Data tracking and logging software was also developed in house. During measurement, sample injection was achieved by switching 3-way mini valve feeding port from baseline-solution (1) to sample container (2). After sample injection, peak heights were determined by software and converted to concentration by using calibration curve built from standard solutions

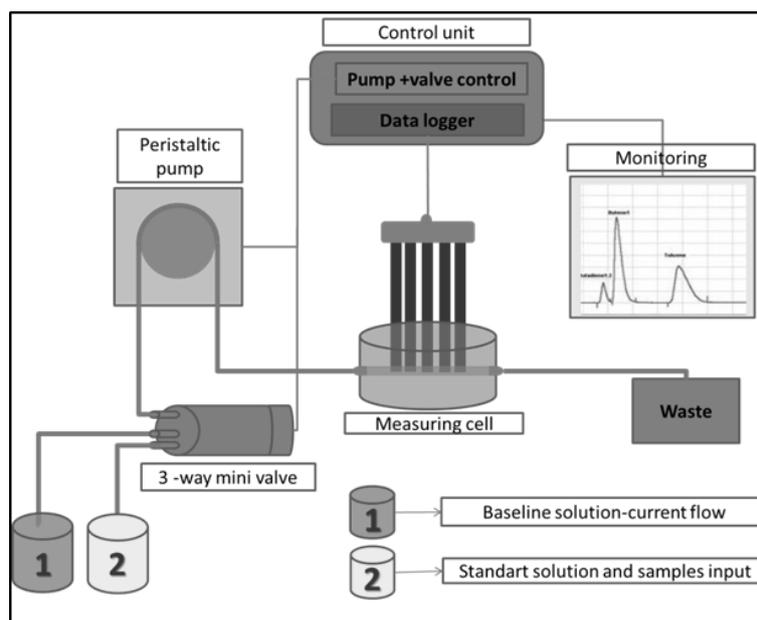


Figure 2. The scheme of the flow injection analysis system (Soil Analysis System)

Since ion-selective electrodes operates in a limited pH range, an appropriate extraction solution was developed for the system. Developed extraction solution allowed simultaneous extraction of macro nutrient elements ( $K^+$ ,  $Ca^{2+}$ ,  $NH_4^+$ ,  $NO_3^-$ ) in 13 minutes. Extraction parameters are given in Table 1. After extraction step, simultaneous measurement of nutrient elements was achieved with flow injection analysis system.

Table 1. Extraction parameters and optimal conditions for simultaneously extraction of ions

Parameters of extraction	Explanations	
Soil / extraction solution ratio (W/V)	1/5,7	
Extraction time (minute)	13	In orbital Shaker (Stuart, SSL1) with 50 mL Falcon Flask
Karıştırma hızı (rpm)	230	In orbital Shaker (Stuart, SSL1)

Prior to soil sample measurement, calibration curve was derived using standard solutions for  $K^+$ ,  $Ca^{2+}$ ,  $NH_4^+$ , and  $NO_3^-$ .

### Design of soft sensor model for K (potassium) fertilizer recommendation

Soft sensor model employed in the study was an artificial neural network (ANN) model. ANN model had a structure of multilayer feed forward network with a single hidden layer. Sigmoid function was used in hidden layer as the activation function. Back propagation algorithm was used in training of neural network model. In each training step, input vector was fed into neural network model. Output of neural network was calculated and compared with the expected target value. Back propagation algorithm tries to minimize the error between expected and output value by ANN model (Bishop et al., 1995).

Artificial neural network implementation of Weka (Waikato Environment for Knowledge Analysis) software package was used in the study. Weka is a collection of machine learning algorithms implemented as java class libraries (Hall et al., 2009). Matlab R2009a (Mathworks) is also used as a platform for calling Weka methods in different settings and drawing plots.

Evaluation of neural network model performance was based on coefficient of determination ( $R^2$ ) given by formula;

$$R^2 = 1 - \frac{SQR}{SQT}$$

SQR is the sum of squares regressions and SQT is the sum of squared residuals.  $R^2$  values were calculated with ten-fold cross validation method. Data set was randomly divided into ten folds. Each fold was used for validation of neural network model while remainder data was used for training of neural network model. This procedure was repeated for each fold so that 10 different neural networks were developed. Outputs of these networks were averaged and used in calculation of  $R^2$  values which represents generalization performance of neural network model. Generalization is the ability of the neural network to predict outcome of unknown patterns. In training phase, training data is introduced to adjust internal weight structure of the network. Another validation data set is needed to test network's generalization ability. If the network produces acceptable predictions close to accuracy obtained in training phase, it is said to generalize well (Hastie et al., 2011).

An optimum subset of input vector set was determined by measuring performance of all possible combinations with a predefined neural network architecture. Input combinations were sorted according to calculated  $R^2$  values and 30 best combinations were taken into account for selection of variables. Frequency of each variables was determined and frequency with greater than 80 % were picked.

Number of neurons in the hidden layer, momentum value and learn-rate parameters of NN model was optimized by direct search method. Number of neurons in the hidden layer is related to the complexity of the neural network model. Momentum parameter determines update ratio of coefficients in each training step. Similarly, learning rate defines each input vector's singular impact on changing weight and bias coefficients of neural network structure. Finally, optimized neural network structure was used in calculation of fertilizer ( $K_2SO_4$ ) recommendation for different plants. Relative error between measured potassium (K) and soft sensor measurement was calculated by;

$$E = \frac{y_{conventional} - y_{soft}}{y_{conventional}}$$

Where  $y_{conventional}$  denotes classic measurement,  $y_{soft}$  denotes soft sensor measurement.

## Results and Discussion

Artificial neural network model approach is essentially a data driven method so appropriate selection of input variables is a very important step in developing the model. Number of total variables available for training was 10 so there were  $2^{10} = 1024$  different combinations. A neural network model for each combination were developed with 8 neurons in the hidden layer, momentum of 0.3 and 0.1 learn rate.

Corresponding  $R^2$  values for each subset was calculated using cross-validation and 30 best combinations listed in Table 2.

Table 2. Calculated  $R^2$  values for different subset combination of input measurements

Subset No	K	Ca	NO <sub>3</sub>	NH <sub>4</sub>	Sand	Clay	Silt	pH	EC	Lime	R <sup>2</sup>
1	+	+	+	+	+	+	-	+	+	+	0,887093
2	+	+	+	+	-	+	+	+	+	+	0,886932
3	+	+	+	+	+	+	+	+	+	+	0,88503
4	+	+	+	+	+	-	+	+	+	+	0,881879
5	+	+	+	+	+	+	+	-	+	+	0,877828
6	+	+	+	+	+	+	+	+	+	-	0,869824
7	+	+	+	+	+	-	+	+	+	-	0,867503
8	+	+	+	-	-	+	+	+	+	+	0,865235
9	+	+	+	+	+	+	-	+	+	-	0,86461
10	+	+	+	+	+	-	+	-	+	+	0,86411
11	+	+	+	+	+	+	-	+	-	-	0,861884
12	+	+	+	-	+	+	+	+	+	+	0,860601
13	+	+	+	+	+	+	-	+	-	+	0,860027
14	+	+	+	+	-	+	+	+	+	-	0,85999
15	+	+	-	+	+	-	+	+	+	+	0,859795
16	+	+	+	+	+	+	-	-	+	+	0,85909
17	+	+	+	-	-	+	+	+	+	-	0,859011
18	+	+	+	+	+	+	+	+	-	+	0,858734
19	+	+	-	+	+	+	-	+	+	+	0,858585
20	+	+	-	+	+	+	+	+	+	-	0,857944
21	+	+	+	-	+	+	-	+	+	-	0,857716
22	+	-	+	+	+	+	+	+	+	+	0,857445
23	+	-	+	+	+	+	-	+	+	-	0,857343
24	+	+	-	+	-	+	+	+	+	+	0,856046
25	+	+	+	+	-	+	-	+	+	+	0,855976
26	+	+	-	+	+	+	+	+	+	+	0,855522
27	+	+	+	+	+	+	+	-	-	+	0,854616
28	+	+	+	-	+	+	-	+	+	+	0,853762
29	+	+	+	+	-	+	+	-	-	+	0,85367
30	+	+	+	+	-	+	+	-	+	+	0,853602
Frequency	30	28	25	25	22	26	20	24	25	21	
Frequency	100	93,3	83,3	83,3	73,3	86,7	66,7	80,0	83,3	70,0	86,3

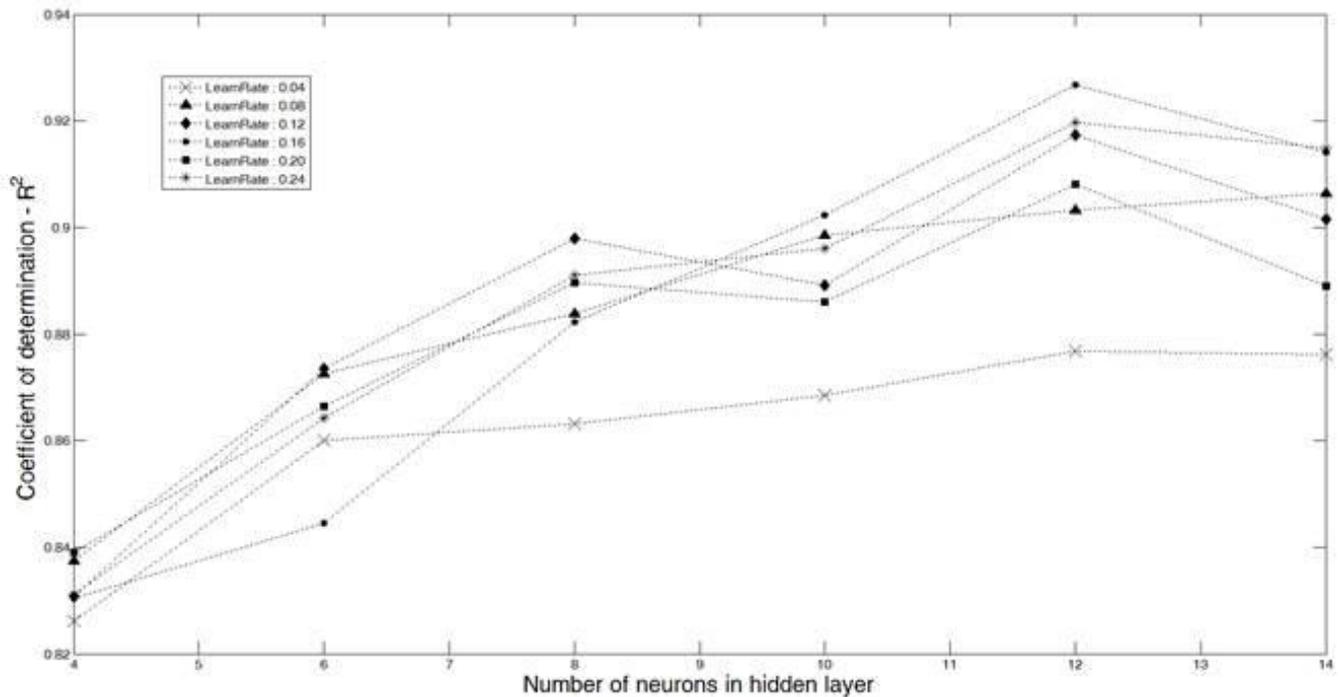
Frequency of each variable were also presented. As anticipated, K –ISE measurement came out in all subsets. Calcium (Ca<sup>2+</sup>) also had a higher occurrence than other electrode measurements, namely NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. A threshold value of 80% were set and variables with frequency of 80% discarded. In soil property measurements only clay was selected. In summary, 7 of 10 variables (K<sup>+</sup>, Ca<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Clay, pH, EC) were chosen as soft sensor input variables (Table 3).

Table 3. Chemical and physical characteristic of soil parameters which were chosen as software sensor input

Parameter*	pH (1:1)	EC (1:1) dSm-1	Clay %	Total N, %	K, cmol.kg-1	Ca, cmol.kg-1
Minimum	4,48	0,13	2,9	0,046	0,085	6,39
Maximum	7,92	1,86	69,5	0,454	2,169	44,658
Avarege	6,59	0,45	40,7	0,16	0,465	18,207
Median	6,73	0,42	40,7	0,152	0,376	15,398

\*pH 1:1 (soil:water); EC 1:1 (soil:water); Soil texture, Bouyoucos Hydrometer method; Total N, Kjeldahl Method; K, Ca, 1 N NH<sub>4</sub>OAc extraction method.

Optimization of neural network structure was accomplished by calculating R<sup>2</sup> values for various parameters and picking the parameter set with highest R<sup>2</sup>. Momentum rate is varied between 0.1 and 0.4, learn rate was varied between 0.04 and 0.24, number of neurons in the hidden layer was varied between 2 and 14. Calculated R<sup>2</sup> values for various learn rate and neuron count are presented in Figure 2.

Figure 2. R<sup>2</sup> Values for different neuron count and learn rate

Optimum point was found to be with 12 neurons in the hidden layer, momentum rate of 0.3 and learn-rate of 0.16. It was observed that for different learn-rate values, relatively highest R<sup>2</sup> values were obtained with neural network models of 12 neurons in the hidden layer.

In Figure 3, relation between observed values and soft sensor prediction based on neural network model is illustrated. Calculated R<sup>2</sup> value of 0.927 demonstrated that soft sensor approach provide reasonably reliable predictions.

Finally, validity of soft sensor results were demonstrated by utilizing soft sensor measurement results of available K in fertilizer recommendation and comparing to recommendations calculated with traditional soil analysis. Relative error in percentage was calculated by following formula

$$\text{Relative error in recommendation} = \frac{(f_{\text{soft sensor}} - f_{\text{conventional}})}{f_{\text{conventional}}} * 100$$

where  $f_{\text{soft sensor}}$  is fertilization recommendation for K calculated by soft sensor measurement and  $f_{\text{conventional}}$  is fertilization recommendation calculated by traditional analysis method. In Figure 4 a,b,c relative error of fertilizer recommendation is given for tomato, potato and corn. For tomato and potato, mean of absolute relative error is found to be %2.2. Maximum of relative potassium fertilizer recommendation error for both of these plants were below %8 which indicated that soft sensor system exhibited excellent match with

traditional analysis. For corn mean error was higher with a value of 6.8%. Although maximum absolute error was 58%, there were only 5 sample with errors higher than 20% therefore these results were also acceptable.

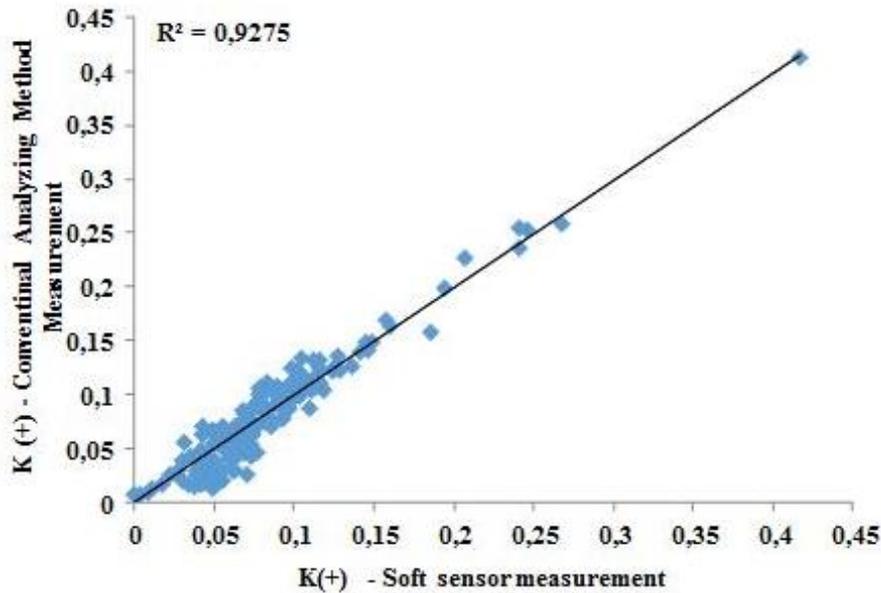


Figure 3. Comparison of soft sensor measurements with conventional analysis result

## Conclusion

In this article, a soft sensor system composed of flow-injection analysis and artificial neural network model is presented in the context of its application in fertilizer recommendation. A full factorial approach was employed for selection of soft sensor inputs. Artificial neural network structure was also rigorously optimized. Both comparison of soft sensor outputs with reference laboratory results and potassium fertilizer recommendations based on outputs demonstrated that developed soft sensor system is a viable alternative to traditional soil analysis methods.

The significant benefit of developed system is the capability of getting rapid results on the field. Soft sensor models for predicting concentration of  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  can be developed in a similar manner, and proposed soil analysis system can be used for fertilizer recommendation of other nutrient elements.

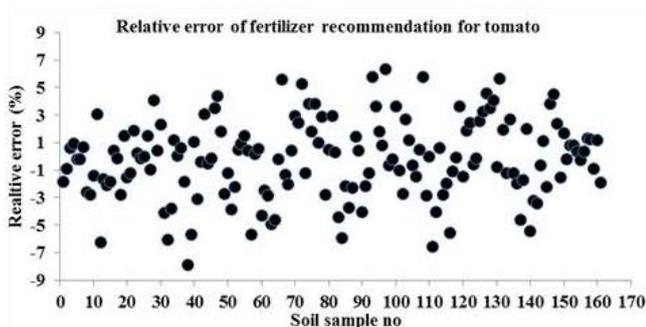


Figure 4a. Comparison of soft sensor measurements with conventional analysis result for tomato

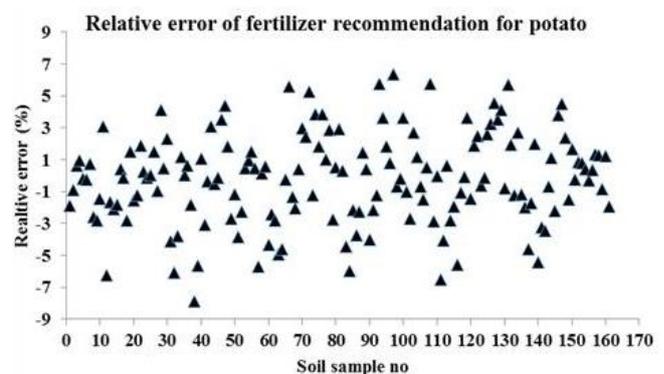


Figure 4b. Comparison of soft sensor measurements with conventional analysis result for potato

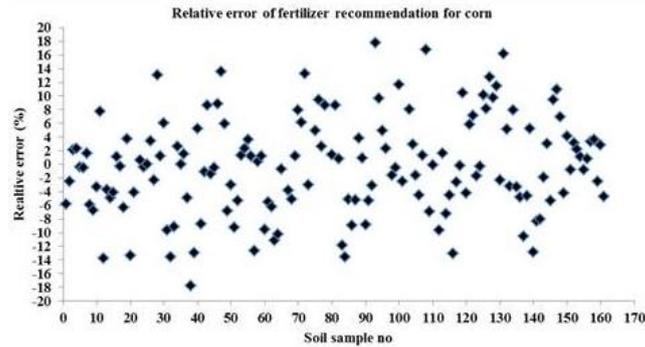


Figure 4c. Comparison of soft sensor measurements with conventional analysis result for corn

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